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Modification of PVC and PVC Copolymer by Substitution Imide Groups

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Abstract

In this work the poly vinyl imides were prepared as thermally stable polymers by modified PVC and PVC copolymers with different cyclic imides such as naphtha imide, phthal imide, male imide and succin imide as a pendant groups.

This method gave new polyimides, from considered especially plastic because of their outstanding high performance properties. As such, they are priced well above commodity polymers such as PVC and PVC copolymers.

All the prepared polymers were characterized by IR, UV spectroscopy, elemental analysis and chemical reactions, and thermal analysis such as DTA and TG. Physical properties and the viscosities for all prepared polyimides were determined by using DMF as a solvent. This method gave good results and the new modification of PVC thermoplastic polymer to the PVC-link with different imides gave higher thermally stable polymers compaired with the origin PVC polymer.

Introduction

Polyimides are condensation polymers derived from bifunctional carboxylic anhydrides and primary diamines. They contain the imide structure (-CO-NR-CO-) as a linear or heterocyclic unit along the main chain of the polymer backbone. Aromatic heterocyclic polyimides exhibit outstanding mechanical properties and excellent thermal and oxidative stability, and are of major commercial and industrial importance (1-4).

These materials are widely used in place of metals and glass in high performance applications through the electrical, electronics automotives aerospace and packaging industries. The condensation of aromatic diimide with aliphatic dihalides is a novel alternative to the preparation of polyimides from aromatic dianhydrides and aliphatic diamines (5,6).

A dipolar aprotic solvent is used and catalytic or stochiometric amount of base such as triethylamine, typical temperatures are between 100 and 150 °C. although the reactions are fast, this method produces low molecular weight polymer and cannot be employed for aromatic halides. By an alternative route, the alkali metal salt of the diimide is treated with an aliphatic dihalide in a dipolar aprotic solvent such as DMF giving higher reaction rates but low molecular weights (7,8). The later may be due to insolubility of the polyimides in the reaction solvent. This is a common problem for solvent-based polymerization processes for the preparation of crystalline or insoluble polyimides (9,10).

Experimental

1.Modification of poly vinyl chloride to poly vinyl imide (N_1-N_4):

Four types of modified PVC were prepared from reaction of PVC with different heterocyclic imides by elimination of HCl molecules with pyridine as a catalyst, according to the following procedure:

In a (100 ml) two-necked flask equipped with a magnetic stirrer, dropping funnel and reflux condenser were placed (2 g, 0.29 mole) of PVC with (15 ml) of DMF solvent. The mixture was stirred all the PVC had been dissolved, (3 g, 0.29 mole) of maleimide dissolved in DMF .(3-4 g) pyridine was added gradually through the dropping funnel drop-wise. After about (3 hrs) of reflux a precipitate was separated , filtrated & washed with the solvent and precipitated from DMF, then filtered and dried at 50 °C in vacuum oven. Table (1) lists the physical properties of the prepared modified PVC with pendant imide groups such as maleimide, succinimide, phthalimide and naphthalimide as follow:

2.Modification of vinyl chloride copolymer to polyimide (N_5-N_8):

Four types of modified PVC copolymers were modified to stable imides by elimination of HCl molecules by using pyridine, according to the following procedure:

In a (100 ml) round-bottom flask equipped with reflux condenser a mixture of (2 g, 0.013 mole) of PVC copolymer with (20 ml) of pure DMF. The mixture was stirred until a homogeneous solution was obtained.

A mixture (1.3 g, 0.013 mole) of succinimide and (3 g) pyridine was added to reaction mixture refluxed for (3 hrs) with stirring, then cooled the polymer was precipitated by adding(50 ml) of CCl_4 to reaction mixture,filtered and washed several times and dried in vacuum oven at 50 °C. Table (2) lists the physical properties for all modified PVC copolymer with maleimide, succinimide, phthalimide and naphthalimide as follow:

Results and discussion

A large number of structurally modified poly imides have been developed in recent years for specific applications, particularly composites for the aerospace industry, where the need for materials with high temperature capabilities for prolonged periods and resistance to aggressive solvents is crucial, other necessary properties include strength and low flammability, to meet these demanding requirements, for there the new method of converting thermoplastic polymers to the thermal more stable polymers were investigated in this work.

PVC and PVC copolymers were allowed to react with different imides in dry DMF and a good conversion % of corresponding imides were obtained by using pyridine for removing HCl molecules as in scheme (1):

The new modified polymers were characterized and structural determined by using IR, UV, elemental analysis and thermal analysis were studied.

IR spectra of N_1 modified PVC with maleimide, Fig. (1), shows absorption bands at 2960 cm^{-1} due to (C-H) aliphatic, and at 1650 cm^{-1} and 1780 cm^{-1} for (C=O) imide, and at 1220 cm^{-1} for (C-N), tables (3&4) list the IR absorptions for prepared polymers (N_1- N_8).

UV spectra of polymers (N_1 and N_3) show the λ_{max} at 304 nm and 320 nm due to (π-π*) transition, as in Fig. 4 and 5.

Elemental analyses of the modified polymers were list in table 5 and from N, Cl %, which used for calculate the modified % for all prepared polymers before and after modification , All prepared polymers were estimated their viscosities using DMF solvent at 30 °C, which ranged (0.79-09), also Tg analysis as in Fig. (6) shows the thermal stability of modified PVC that due to the imide as apendant groups through the back-bone of polymer, in addition of easy modified PVC when compared with other oldest methods of preparation polyimides (11,12).

We were able to modify poly (vinyl chloride) (PVC) by introducing imides moieties through halogen displacement reaction, thus modified showed improved overall thermal stability and interesting changes relative to unmodified PVC. The facile chlorine displacement from PVC indicated the possibility of easy anchoring imide to PVC matrix.

Fig. (6) presents the thermograms of the various PVC link with imides (N_1-N_4) along with the one for unmodified PVC. The initial decomposition temperature of unmodified PVC (Ca. 250 °C) is somewhat lowered in the modified PVC-imide. However, it is possible that this small weight loss about 10% is due to loss of solvent/water from the modified matrix. Beyond Ca 250-350 °C (20-30% weight loss), PVC link with imides start gaining in stability in the order:

$$PVC < N_1 < N_2 < N_3 < N_4$$

The presence of aliphatic imides such as N_1 and N_2 reduced thermal and oxidative stabilities, but the aromatic imides such as N_3 and N_4 were higher thermal stabilites with lower decomposition rates tend to decompose over a broader temperature range.

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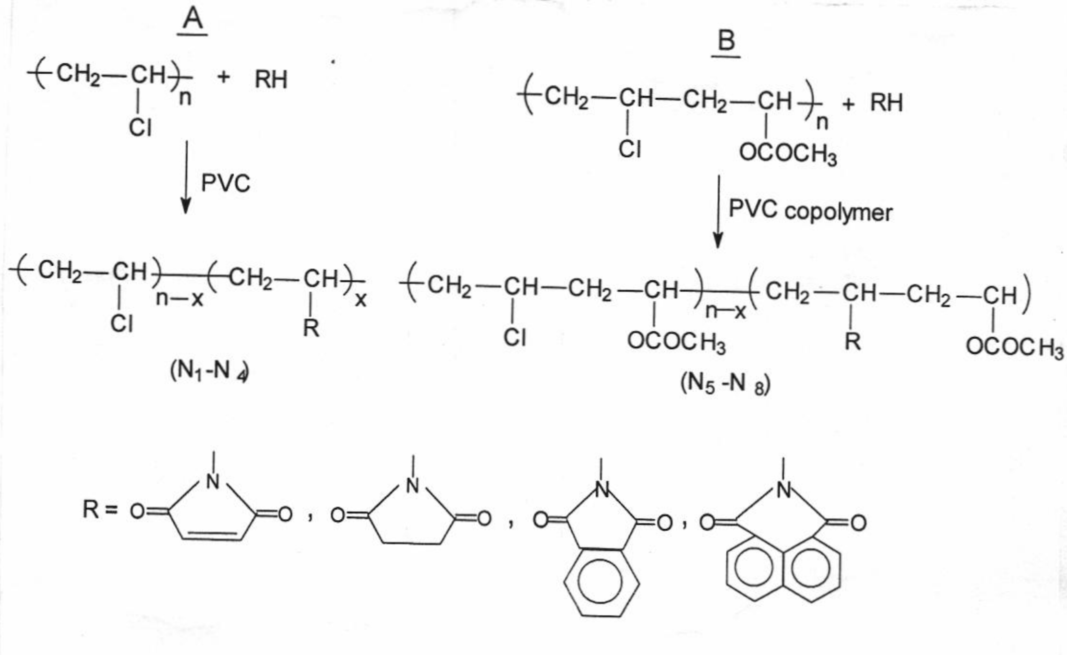
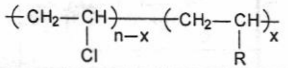


Scheme [1]

Table (1): Physical properties of prepared modified PVC with imide group (N_1-N_4).



$$\left(CH_2-\underset{Cl}{CH}\right)_{n-x}\left(CH_2-\underset{R}{CH}\right)_x$$

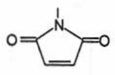
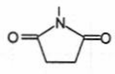
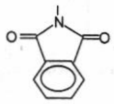
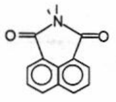
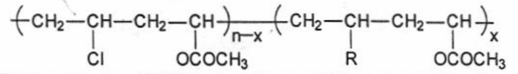
Comp. No.	R	Color	[η] dL/g	Modification (%)	Softening point °C
N_1		Brown	0.81	42	335-340
N_2		Black	0.93	66	310-320
N_3		Brown	0.79	70	>350
N_4		Dark brown	0.86	54	>350

Table (2): Physical properties of prepared polymers (N_5-N_8)



$$\left(CH_2-\underset{Cl}{CH}-CH_2-\underset{OCOCH_3}{CH}\right)_{n-x}\left(CH_2-\underset{R}{CH}-CH_2-\underset{OCOCH_3}{CH}\right)_x$$

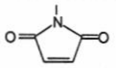
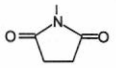
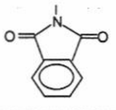
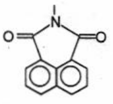
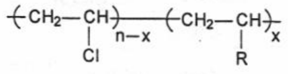
Comp. No.	R	Color	[η] dL/g	Modification (%)	Softening point °C
N_5		Dark brown	0.82	56	>350
N_6		Brown	0.87	48	>350
N_7		Black	0.90	45	>350
N_8		Brown	0.84	62	>350

Table (3): IR absorption of prepared polymers (N_1-N_4)



$$\left(CH_2-\underset{Cl}{CH} \right)_{n-x} \left(CH_2-\underset{R}{CH} \right)_{x}$$

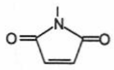
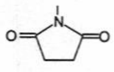
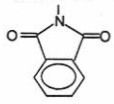
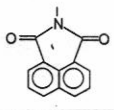
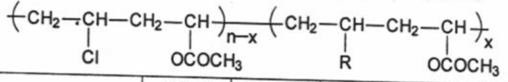
Comp. No.	R	ν(C-H) alkane (cm^{-1})	ν(C=O) (cm^{-1})	ν(C-N) (cm^{-1})	ν(others) (cm^{-1})
N_1		2960	1700	1220	(C=C) alkene 1570
N_2		2960	1700	1240	-
N_3		2980 2920	1750	1220	(C=C)ar. 1510 (C-H)ar. 3080
N_4		2970	1780	1210	(C=C)ar. 1530 (C-H)ar. 3080

Table (4): IR absorption of prepared polymers (N_5-N_8)



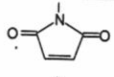
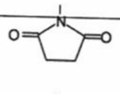
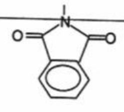
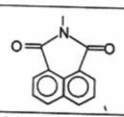
Comp. No.	R	ν(C-H) alkane (cm^{-1})	ν(C=O) (cm^{-1})	ν(C-N) (cm^{-1})	ν(C-O) (cm^{-1})	ν(others) (cm^{-1})
N_5		2980	1660 1700 1780	1210	1300	(C=C) 1570
N_6		2970	1680 1720 1770	1190	1310	-
N_7		2960	1690 1748 1780	1220	1300	(C-H)ar. 3080
N_8		2950	1650 1780 1790	1200	1310	(C-H)ar. 3080

Table (5): Elemental analysis of (N, Cl) for prepared polymers

Comp. No.	N%	Cl%
	Before Modification After Modification	Before Modification After Modification
N_2	0.0 19.15	57.43 38.28
N_3	0.0 16.72	56.93 40.21
N_6	0.0 12.40	24.36 11.85
N_7	0.0 13.68	24.17 10.92

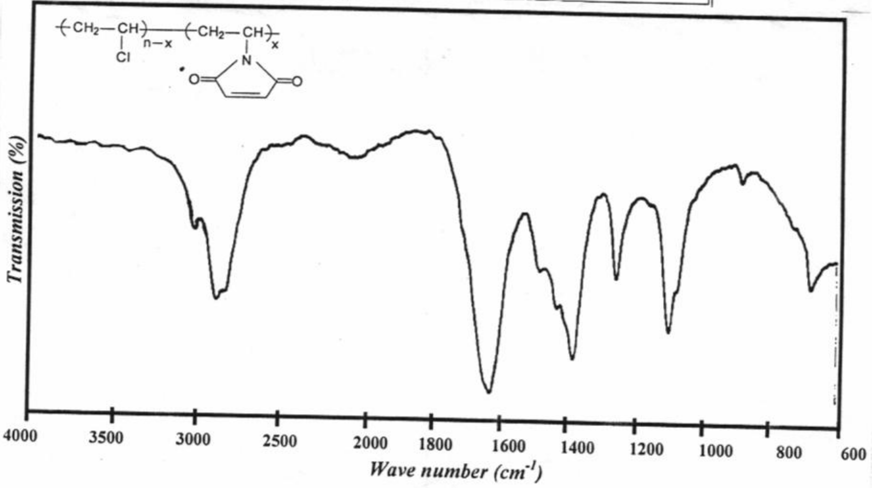


Fig. (1): IR spectra of N_1

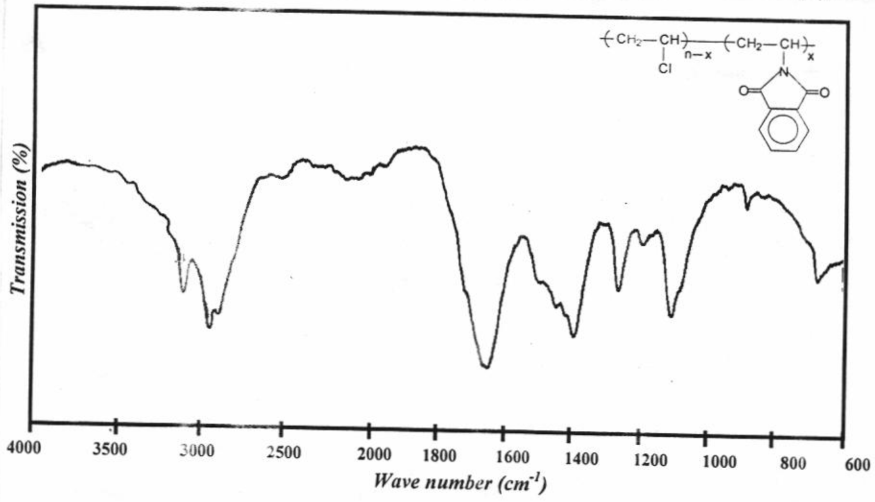


Fig. (2): IR spectra of N_3

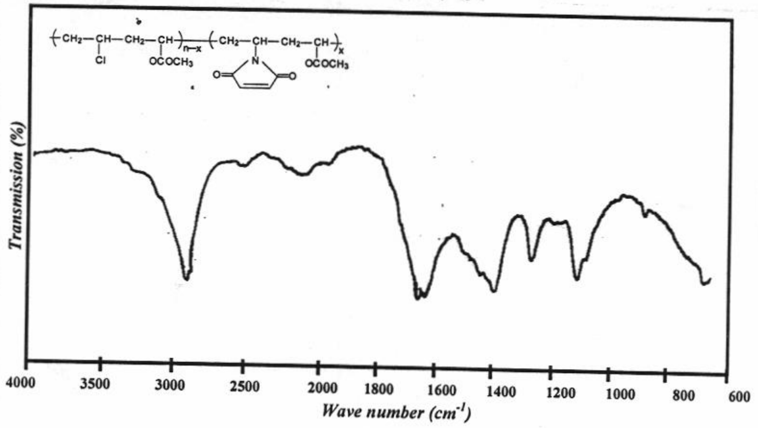


Fig. (3): IR spectra of N_5

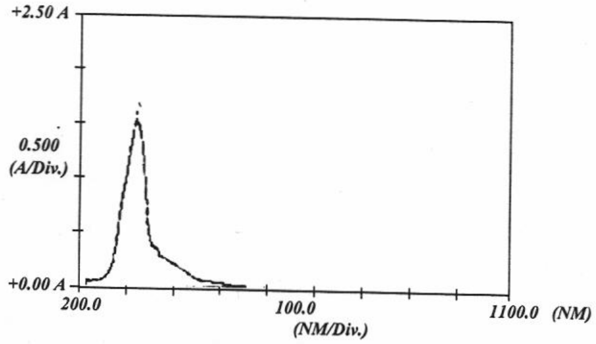


Fig. (4): UV spectra of N_1

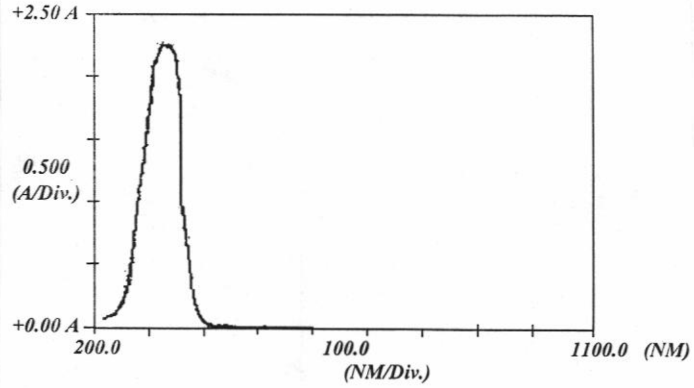


Fig. (5): UV spectra of N_3

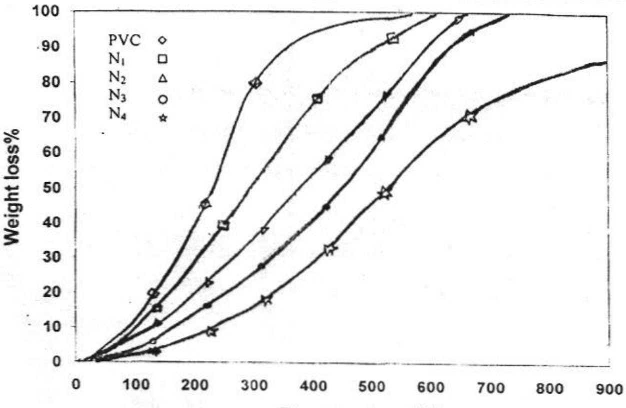


Fig. (6) Weight loss-temperature curves for PVCimides

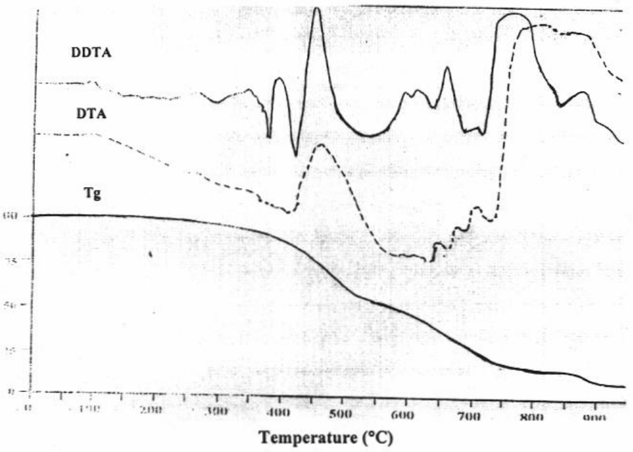


Fig. (7): Tg and DTA thermal analysis of polymer N_2

تحوير بولي كلوريد الفاينيل وبولي كلوريد الفاينيل المشترك بتعويضه بمجاميع الإيمايد

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الخلاصة

تضمن البحث تحضير بعض أنواع البولي فاينيل إيمايد المستقرة حرارياً وذلك بتحوير بولي كلوريد الفاينيل و بولي كلوريد الفاينيل المشترك، مع الإيمايدات الحلقية المختلفة مثل المالي ايمايد والسكسن ايمايد والفثال ايمايد والنفثال إيمايد كمجاميع متدلية ضمن البوليمر الأصلي. هذه الطريقة أعطت بوليمرات الإيمايد التي تعتبر من البوليمرات الخاصة لأنها حضرت بمواصفات عالية من بوليمرات تجارية مثل PVC و PVC المشترك.

شخصت البوليمرات المحضرة بواسطة الأشعة فوق البنفسجية، الأشعة تحت الحمراء، تحليل العناصر والكشوفات الكيميائية، وأجريت لها التحاليل الحرارية مثل التحليل الوزني والتحليل الحراري التفاضلي، وقيست الصفات الفيزياوية لها، وقد قيست اللزوجة الجوهرية باستعمال الداي مثيل فورماميد مذيباً. هذه الطريق أعطت نتائج جيدة من تحوير PVC البوليمر اللدن حرارياً إلى بوليمرات الإيمايد الثابتة حرارياً عند تعويضه بمجاميع الإيمايد المختلفة وبمقارنتها مع البوليمر الأصلي PVC.والتي يمكن استخدامها في مجالات صناعية مختلفة.